feature present, in addition to the spherulites, is the transcrystalline region growing from both polymer-glass interfaces. This is a frequently observed structure which has been shown to consist of sectors of spherulites originating from surface nucleation.[4,5] The cross-sectional view of these rod-like structures accounts for the continuous grainy field seen on viewing through the melt. It is also quite evident from these photomicrographs that the spherulites grow from an optically structureless background. The observations concerning focusing noted above are also explained by these findings.

In Kel-F it was observed[2] that the x-ray crystallinity increased more rapidly than the spherulitic volume measured microscopically. This situation may be explained by the above findings since the measured crystallinity is derived from both the spherulites and the transcrystalline regions.

References

(1) Hawkins, S. W., and Richards, R. B., *J. Polymer Sci.*, 4, 515 (1949).

(2) Price, F. P., *J. Am. Chem. Soc.*, 74, 311 (1952).

(3) Bryant, W. M. D., Pierce, R. H. H., Jr., Lindegren, C. R., and Roberts, R., *J. Polymer Sci.*, 41, 131 (1955).

(4) Jenckel, E., Teege, E., and Hinrichs, W., *Kolloid Z.*, 129, 19 (1952).

(5) Barriault, R. J., and Gronholz, L. F., *J. Polymer Sci.*, 18, 393 (1955).

BRUCE B. BURNETT
W. F. McDEVIT

Carothers Research Laboratory
E. I. du Pont de Nemours and Co.
Experimental Station
Wilmington, Delaware

Effect of the Size of Acyl Chain on Copolymerization of Vinyl Esters

Previously[1] we reported that the monomer reactivity ratios for the system vinyl palmitate-vinyl acetate at 70°C. were 0.78 and 1.15 based on polymer analysis, or 0.66 and 0.84 based on analysis of residual monomer. Because the monomer reactivity ratios are both approximately 1, it may be concluded that the free radical formed from each monomer reacted essentially non-preferentially with either monomer and that, therefore, the long acyl chain has little or no effect on the kinetics of propagation in copolymerization. In order to verify this, the monomer reactivity ratios for vinyl stearate and several monomers were determined. The results are listed in Table I and are compared with values reported in the literature for vinyl acetate and these monomers.

TABLE I

COMPARISON OF r VALUES FOR VINYL STEARATE AND FOR VINYL ACETATE

Comonomer (M_2)	Vinyl stearate (M_1)			Vinyl acetate (M_1)			
	Temp., °C.	r_1	r_2	Temp., °C.	r_1	r_2	Refs.
Vinyl acetate	70	0.73	0.90	—	—	—	—
Diisopropyl maleate	70	0	0.0075	60	0.17	0.043^a	3
Methyl acrylate	70	0.03	5.8	60	0.1	9	4
Acrylonitrile	70	0.03	4.3	60	0.061	4.05	4
				70	0.07	6	5

^{a} Diethyl maleate.

Copolymerization was carried out in bulk using azobisisobutyronitrile as a catalyst at 70°C. The conversion was kept below 10%, and a wide range of monomer mixtures was used in order to minimize the errors arising from changes in the monomer composition. The composition of the copolymers was determined from their carbon contents or, in the case of acrylonitrile, from the nitrogen content. Monomer reactivity ratios were determined by the method of Fineman and Ross.[2]

The data of Table I show that in copolymerization, vinyl acetate and vinyl stearate behave almost identically. The reactivity of both the monomer and of the radical are thus apparently unaffected by the length of the acyl chain.

References

1. W. S. Port, E. F. Jordan, Jr., J. E. Hansen, and D. Swern, *J. Polymer Sci.*, **9**, 493 (1952).
2. M. Fineman and S. D. Ross, *J. Polymer Sci.*, **5**, 259 (1950).
3. F. M. Lewis and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1533 (1948).
4. F. R. Mayo, C. Walling, F. M. Lewis, and W. F. Hulse, *J. Am. Chem. Soc.*, **70**, 1523 (1948).
5. T. Alfrey, Jr., J. Bohrer, H. Haas, and C. Lewis, *J. Polymer Sci.*, **5**, 719 (1950).

LEE P. WITNAUER
NATHANIEL WATKINS
WILLIAM S. PORT

Eastern Regional Research Laboratory
Eastern Utilization Research Branch
United States Department of Agriculture
Philadelphia 18, Pennsylvania